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STRUCTURE OF GLASSES IN THE $\text{Na}_2\text{O} - \text{Fe}_2\text{O}_3 - \text{B}_2\text{O}_3 - \text{SiO}_2$ SYSTEMI. N. Dvornichenko¹ and S. V. Matsenko¹Translated from *Steklo i Keramika*, No. 1, pp. 11–13, January, 2000.

The structure of glasses of a local area of the $\text{Na}_2\text{O} - \text{Fe}_2\text{O}_3 - \text{B}_2\text{O}_3 - \text{SiO}_2$ system is studied. The sequence of formation of oxygen-containing tetrahedral groups in the presence of nonbridge oxygen ions is established. Formation of groups of a six-coordinated iron cation facilitates crystallization of sodium-boron-silicate glass melts in cooling.

Studies of the coordination state of iron ions in boron-silicate glasses are of great interest [1, 2]. It is known [3] that iron ions, depending on their coordination, are able either to participate in the glass-skeleton structure or to modify this structure. According to published data [3–5], Fe^{3+} cations in glasses can exist in tetrahedral and octahedral coordination, and Fe^{2+} cations exist in octahedral coordination. Similarly to the aluminum coordination effect [5], the structural arrangement of iron cations in glasses containing Na_2O is determined by the ratio $\text{Na}_2\text{O} : \text{Fe}_2\text{O}_3$. With the ratio $\text{Na}_2\text{O} : \text{Fe}_2\text{O}_3 > 1$, all Fe^{3+} cations exist in tetrahedral coordination and take part in glass formation. With the ratio $0 < \text{Na}_2\text{O} : \text{Fe}_2\text{O}_3 < 1$, some of the cations have octahedral coordination, and the others have tetrahedral coordination.

It is obvious that with the simultaneous presence of iron and boron cations, the sequence of formation of $[\text{BO}_4]$ or $[\text{FeO}_4]$ tetrahedra will determine the glass structure. According to the boron coordination effect [5], boron cations, depending on the ratio $\text{Na}_2\text{O} : \text{B}_2\text{O}_3$, can have 3 or 4 coordination number. However, in contrast to the ratio $\text{Na}_2\text{O} : \text{Fe}_2\text{O}_3 = 1$, needed for formation of iron tetrahedra, the ratio $\text{Na}_2\text{O} : \text{B}_2\text{O}_3$ that determines complete conversion of boron cations to tetrahedral coordination in boron silicate glasses has to be greater than 1. In the opinion of A. A. Appen [5], this is related to the distribution of part of the introduced sodium oxide in the silica phase of the glass. Since Fe_2O_3 is isomorphic with respect to Al_2O_3 , one can expect that glasses in the system considered will exhibit a coordination effect similar to the alumino-boron effect. However, the sequence of formation of tetrahedra by iron and boron cations has so far not been precisely established.

According to data in [1], the ability of Si^{4+} , Al^{3+} , B^{3+} , and Fe^{3+} cations to form tetrahedral groups is as follows: $\text{Si}^{4+} \rightarrow \text{Al}^{3+} \rightarrow \text{Fe}^{3+} \rightarrow \text{B}^{3+}$. Fe^{3+} cations are the first to con-

vert to tetrahedral coordination compared to boron cations, since the ratio of ionic radii $R_c^{n+} : R_o^{2-}$ for Fe^{3+} cations is two-fold closer to the limiting values of the interval required for coordination number 4 (0.225–0.414) than for B^{3+} cations. In order to convert Fe^{3+} cations to tetrahedral coordination, the ratio $\text{Na}_2\text{O} : \text{Fe}_2\text{O}_3 = 1$ is required, and for B^{3+} cations, the ratio $\text{Na}_2\text{O} : \text{B}_2\text{O}_3$ should be equal to or greater than 1.5.

According to V. I. Skorospelova and S. A. Stepanov [3], boron cations win the competition for nonbridge oxygen ions introduced with an alkali oxide and are the first to form tetrahedra.

In the case of producing a glaze coating, the reaction between three-coordinated boron atoms and Fe_2O_3 is absent [3]. Thus, according to IR spectra of these glazes, introduction of Fe_2O_3 (up to 16 wt.%) does not affect the content of three-coordinated and, consequently, four-coordinated boron atoms.

The purpose of the present paper was to study the structural state of iron and boron cations in some glasses of the $\text{Na}_2\text{O} - \text{Fe}_2\text{O}_3 - \text{B}_2\text{O}_3 - \text{SiO}_2$ system. The chemical composition of the glasses is given in Table 1.

Glass mixtures were prepared from “chemically pure” reactants, including soda ash, boric acid, ferric oxide (Fe_2O_3), and quartz sand. The glasses were melted from a 200 g mixture in a silite furnace at a temperature of 1300°C

TABLE 1

Glass composition	Molar content (synthesis), %			
	Na_2O	Fe_2O_3	B_2O_3	SiO_2
1	21	14	35	30
2	21	7	42	30
3	18	12	30	40
4	18	6	36	40
5	15	10	25	50
6	15	5	30	50

¹ Ukrainian State Chemical-Engineering University, Dnepropetrovsk, Ukraine.

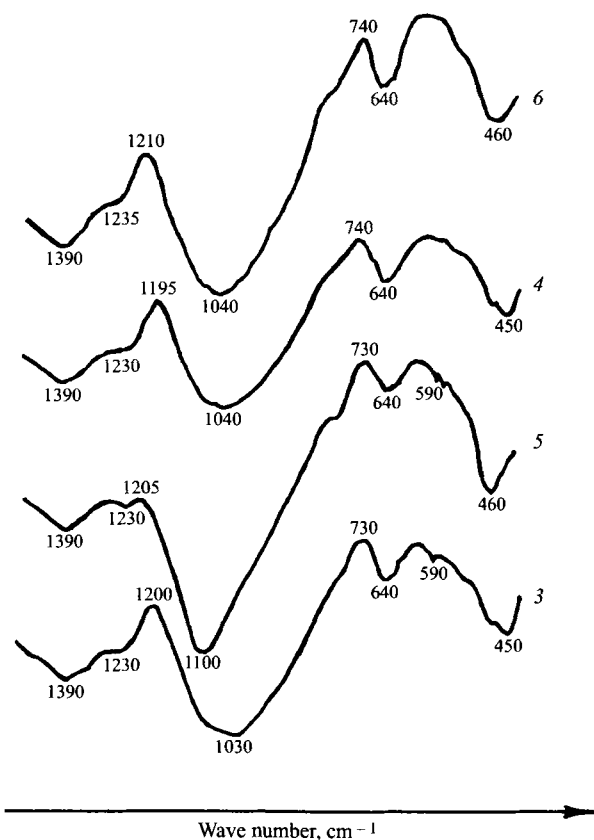


Fig. 1. IR absorption spectra of the studied glasses.

for 20 min. After that the glass melts were subjected to air hardening.

Assuming that the hypothesis of Yu. D. Kruchinin [1] is correct, Fe^{3+} cations in all the glasses considered should be in coordination 4, and in the opinion of V. I. Skorospelova and S. A. Stepanov [2] they should be in coordination 6. However, considering that part of the sodium oxide can be distributed in the silica phase of the glass, it can be assumed that some of the Fe^{3+} cations exist in tetrahedral coordination.

The ability of iron and boron cations to take oxygen off alkali oxides is determined by the following factors. The ionic radii of the cations are 0.60 Å in Fe^{3+} and 0.20 Å in B^{3+} , and their interionic distances are 1.87 and 1.54 Å [1]. The bond energy $E_{\text{Fe}^{3+}-\text{O}}$ and $E_{\text{B}^{3+}-\text{O}}$ is 72 and

144 kcal/mole, respectively [1, 6]. Accordingly, boron ions, which have a smaller ionic radius and a greater bond energy with oxygen than iron ions, form more stable coordination groups.

Assuming that an Fe^{3+} cation cannot take an oxygen ion from a $[\text{BO}_4]$ tetrahedral group and can change over to tetrahedral coordination only due to an excess of Na_2O , we can correlate the amount of Fe_2O_3 and the amount of "excess" Na_2O in the compositions of the glasses considered.

Table 2 shows the ratio $\text{Na}_2\text{O}_{\text{exc}} : \text{Fe}_2\text{O}_3$ and the expected content of boron and iron cation groups in the glasses considered, calculated by the method in [7]. The calculation is carried out based on the known maximum possible content of boron cations existing in tetrahedral coordination $\text{B}_{4\text{max}}$ [7]. The content of B_4 in sodium-borate glasses with the ratio $\text{Na}_2\text{O} : \text{B}_2\text{O}_3$ below 0.75 cannot exceed 43% of the total boron content and is found from the ratio $\text{B}_{4\text{max}} : \text{B}_{\text{tot}} = 0.428R$.

It is assumed that after formation of 43% boron tetrahedra, the remaining oxygen atoms go to formation of iron tetrahedra. If free oxygen atoms still remain after that, the possibility of a larger amount of tetrahedral boron groups being formed arises. This is possible due to their complete potential screening by $[\text{SiO}_4]$ groups.

In studying the structure of glass compositions 3 – 6 using the IR-spectroscopy method, it was found that this structure is rather complex and is determined by the presence of boron ions in coordination three and four and iron ions in coordination four and six (Fig. 1).

Formation of $[\text{Fe}^{3+}\text{O}_4]$ tetrahedra is evidenced by the fact that the IR spectra of the glasses exhibit an absorption band at 640 cm^{-1} , which is typical of $[\text{Fe}^{3+}\text{O}_4]$ coordination groups [8]. Moreover, as the Fe_2O_3 content increases, the maximum of the main absorption band is shifted into a field with a lower absorption frequency (from 1100 to 1030 cm^{-1}), which is also indirect evidence of formation of $[\text{Fe}^{3+}\text{O}_4]$ groups and their incorporation in the silicon-oxygen skeleton of the glass.

According to the data obtained, with the replacement $\text{B}_2\text{O}_3 \rightarrow \text{Fe}_2\text{O}_3$ in the amount of 6% (here and elsewhere molar content is indicated), in addition to a shift of the maximum of the main absorption band, a decrease in its intensity is observed. This corroborates the fact of formation of $[\text{Fe}^{3+}\text{O}_6]$ groups along with a large amount of $[\text{Fe}^{3+}\text{O}_4]$ coordination groups. The IR absorption spectra of glass compo-

TABLE 2

Glass composition	$\text{Na}_2\text{O} : \text{B}_2\text{O}_3$	$\text{B}_{4\text{max}}$	$\text{Na}_2\text{O}_{\text{exc}} : \text{Fe}_2\text{O}_3$	Calculated content of groups				Expected coordination number
				$[\text{BO}_4]$	$[\text{BO}_3]$	$[\text{FeO}_4]$	$[\text{FeO}_6]$	
1	0.6	0.257	0.858	17.99	52.01	24.01	3.99	4, 6
2	0.5	0.214	1.716	28.00	56.00	14.00	—	4
3	0.6	0.257	0.858	15.42	44.58	20.52	3.41	4, 6
4	0.5	0.214	1.716	24.00	48.012	12.00	—	4
5	0.6	0.257	0.858	12.85	37.15	17.15	2.85	4, 6
6	0.5	0.214	1.716	20.00	40.00	10.00	—	4

sitions 3 and 5 exhibit a maximum at 590 cm^{-1} , which, according to data in [9], points to the presence of $[\text{Fe}^{3+}\text{O}_6]$ groups. The absorption at this frequency in glass composition 5 is not clearly defined, which is typical of a lower content of $[\text{Fe}^{3+}\text{O}_6]$ octahedral groups. These results agree with the above calculation (see Table 2).

Based on the IR absorption spectra of the glasses, one can also judge the effect of the substitution $\text{B}_2\text{O}_3 \rightarrow \text{Fe}_2\text{O}_3$ in the amount of 6% on the coordination state of the boron ions. For the glasses containing 40% SiO_2 , this substitution has no effect on the absorption maximum at 1390 cm^{-1} . The decreased absorption intensity at 1230 cm^{-1} points to a decrease in the amount of $[\text{BO}_3]$ groups [8]. This substitution in the glasses containing 50% SiO_2 results in a shift of the absorption maximum from 1235 to 1230 cm^{-1} and in a decrease in its intensity.

For the purpose of identifying the presence of a crystalline phase, the glasses considered were subjected to x-ray phase analysis (Fig. 2).

As can be seen, glass composition 6 is x-ray-amorphous. As the Fe_2O_3 content is increased to 10% (composition 5), small quantities of $\alpha\text{-Fe}_2\text{O}_3$, $\gamma\text{-Fe}_2\text{O}_3$, and $\epsilon\text{-Fe}_2\text{O}_3$ appear in the glass phase. As the silicon dioxide content in the glasses is decreased to 40%, the amount of iron and boron oxides increases. As a consequence, the melts become more prone to liquation, which does not predetermine crystallization but clearly facilitates it. Crystals of $\alpha\text{-Fe}_2\text{O}_3$, $\gamma\text{-Fe}_2\text{O}_3$, and $\epsilon\text{-Fe}_2\text{O}_3$ are present in the vitreous phase of glass compositions 1 and 3.

The analysis of the x-ray diffraction patterns revealed that the magnitude of the peak corresponding to $\alpha\text{-Fe}_2\text{O}_3$ changes in direct proportion to the change in the content of $[\text{Fe}^{3+}\text{O}_6]$ coordination groups in the glass.

Thus, the proposed calculation of the content of coordination groups can be used for glasses of the $\text{Na}_2\text{O} - \text{Fe}_2\text{O}_3 - \text{B}_2\text{O}_3 - \text{SiO}_2$ system with the ratio $\text{Na}_2\text{O}_3 : \text{B}_2\text{O}_3$ below 0.75. Application of this calculation in the synthesis of glass-crystalline materials of the aventurine type will make it possible to reduce substantially the volume of experimental work needed to determine the limiting saturability value in saturation of a melt with ferric oxide.

The sequence of formation of oxygen-bearing tetrahedral groups in the presence of nonbridge oxygen ions has been established for the considered glasses of a local region of the $\text{Na}_2\text{O} - \text{Fe}_2\text{O}_3 - \text{B}_2\text{O}_3 - \text{SiO}_2$ system, which is as follows: $[\text{BO}_4] \rightarrow [\text{FeO}_4] \rightarrow [\text{BO}_4]$. Formation of groups of a six-

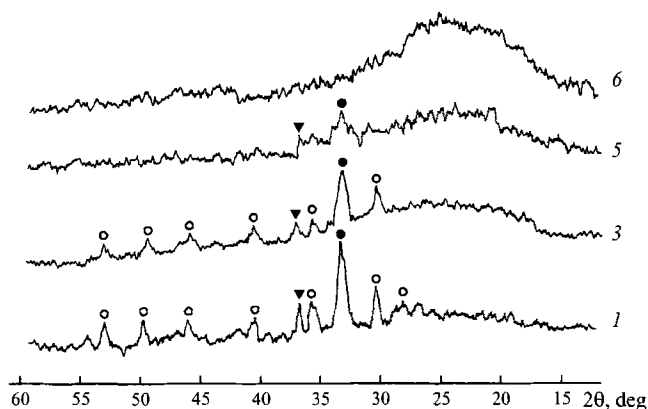


Fig. 2. X-ray diffraction patterns of the studied glasses: ● $\alpha\text{-Fe}_2\text{O}_3$; ○ $\gamma\text{-Fe}_2\text{O}_3$; ▼ $\epsilon\text{-Fe}_2\text{O}_3$.

coordinated iron cation facilitates crystallization of sodium-boron-silicate glass melts in cooling.

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